TRANSLATION:

(19) Japanese Patent Office (JP)

(12) Kokai Patent Gazette (A)

(11) Kokai No.: 3[1991]-115,332

(43) Kokai Date: May 16, 1991

EARLY DISCLOSURE
[Unexamined Patent Application]

(51) Intl. Cl.⁵:	Ident. Code:	Office Ref.:
C 08 J 5/24	CFG	6639-4F
C 32 B 15/08	J	7148-4F
17/00		7148-4F
C 09 D 179/08	PLX	8830-4J

No Examination Requested

Number of Claims: 3 (total: 3 pages)

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(54) Title of the Invention:

METHOD FOR THE PRODUCTION OF PREPREGS AND LAMINATES, AND PRINTED-WIRING BOARDS USING SAID PREPREGS

(21) Application No.: 1[1989]-251,445

(22) Application Date: September 27, 1989

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SPECIFICATION

1. Title of the Invention

METHOD FOR THE PRODUCTION OF PREPREGS AND LAMINATES, AND PRINTED-WIRING BOARDS USING SAID PREPREGS

2. <u>Scope of the Patent Claim(s)</u>:

1. Method for the production of prepregs, characterized in that a glass fabric base material is impregnated with a polyimide resin to the amount of 0.05-30% with respect to the sum of their weights and heated to a semi-cured or cured state; and in that an epoxy resin is applied over said polyimide resin so as to adjust the total resin fraction to 30-80%, then the resulting product is heated to a semi-cured state.

2. Laminates prepared by stacking the necessary number of sheets of the prepreg obtained by the method described in Claim 1, then joining them by the application of heat and pressure.

3. Printed-wiring boards prepared by using the laminates described in Claim 2 as a substrate, perforating this substrate, then applying copper plating to form circuits.

3. <u>Detailed Description of the Invention</u>

Area of Industrial Application

The present invention pertains to a method for the production of prepregs with electrolytic corrosion resistance, and epoxy resin laminates using a glass fabric base material, and to electrolytic corrosion-resistant printed-wiring boards using said prepregs.

Conventional Techniques

As the density of integration of printed-wiring boards has increased, dielectric breakdown due to electrolytic corrosion has become a problem in

printed-wiring boards produced with the use of an epoxy resin laminate using a glass fabric base material. "Electrolytic corrosion" for the purposes of this invention has the following meaning, namely, in actually using an electrical or electronic instrument in which a printed-wiring board with a glass fabric base material is incorporated, conductive materials (mainly copper ions which permeated during plating and copper ions leached from the plated copper) in the substrate migrate from the anode to the cathode through the substrate and precipitate due to the voltage applied from the outside. As this continues, the insulation distance between opposing electrodes gradually becomes shorter, which eventually results in short-circuiting. This phenomenon occurs at the interface between the glass fiber and the resin, and is generally called a CAF (conductive anodic filament). Thermoset resins that contain imide groups are known to generate CAFs far less readily than epoxy resins.

Thermoset resins with imide groups include bismaleimide-based polyimide resins, polyimide resins terminating in nadic acid, polyimide resins terminating in acetylene, totally aromatic polyimide resins, and epoxy-modified polyimide resins. Accordingly, bismaleimide-based polyimide resins and the like tend to be used frequently in substrates for printed-wiring boards which are used in applications that require a high degree of reliability, for example, mainframe computers.

Problems to be Solved by the Invention

However, bismaleimide-based polyimide resins, and for that matter any resins that contain imide groups, are very expensive. For example, commercially available laminates made of these resins alone cost 2-10 times as much as epoxy resin laminates using a fire-resistant glass fabric base material

(NEMA grade FR-4).

In more detail, heating at 200°C or more for 1-3 hours is required in order to heat and pressure form prepregs obtained with the use of a thermoset resin with imide groups, otherwise the desired characteristics can not be obtained. What is more, problems are encountered with respect to working efficiency and yield. As opposed to this, a laminate using a prepreg in which an epoxy resin has been semi-cured can be formed under conditions of 160-180°C, a specified pressure, and a time of 1-2 hours.

The present invention is aimed at providing a method for the production of electrolytic corrosion-resistant prepregs that can be used to produce electrolytic corrosion-resistant epoxy resin laminates using a glass fabric base material, which in turn can be used to produce printed-wiring boards without the problems described above.

An Approach to Solving the Problem

To attain the above-mentioned objective, the present invention is used to produce semi-cured prepregs by impregnating a glass fabric base material with a solution of a thermoset resin that contains imide groups, followed by heating to produce a semi-cured or cured state, and then applying a prescribed amount of an epoxy resin, followed by heating.

The thermoset resin that contains imide groups can be, for example, a bismaleimide-based polyimide resin, a polyimide resin terminating in nadic acid, a polyimide resin terminating in acetylene, or a totally aromatic polyimide resin. A solution prepared by dissolving said resin in a solvent is then used to impregnate the glass fabric base material with said resin in the amount of 0.05-30 parts by weight, and preferably 3-15 parts by weight, rela-

tive to 100 parts by weight of the sum of the glass fabric base material and the resin. This resin-impregnated base material is then heated to obtain a semi-cured or cured state. Optimum resin concentration and drying conditions must be selected, depending on the thickness and the weaving density of the glass fabric, so as not to cause treatment-induced unevenness in the glass fabric base material.

Subsequently, a predetermined amount of a varnish prepared by dissolving an epoxy resin in a solvent is applied to the above-mentioned polyimide resin-impregnated glass fabric base material, then the resulting product is heated to obtain a semi-cured prepreg. A predetermined number of sheets of this prepreg are then stacked and subjected to heat and pressure to obtain a laminate.

Action

As already explained, the CAF phenomenon occurs at the interface between the glass fiber and the resin, but with thermoset resins with imide groups, the CAF phenomenon does not take place anywhere near as easily as with epoxy resins.

The present invention, based on this principle, pertains to a method by which the surface of the glass fiber is evenly covered with a polyimide resin, and then covered with an epoxy resin. Using this method, the results are close to those obtained with just a polyimide resin treatment.

ACTUAL EXAMPLES

Actual Example

A varnish prepared by dissolving a polyimide resin (Kelimide 601; Japan

Polyimide Co.) was applied to an aminosilane-treated glass fabric base material, i.e., MIL7628, so as to give an amount of resin as indicated by 10 relative to the sum of weights of the glass fabric base material and the resin as indicated by 100, then the coated base material was dried by heating. Next, a varnish that contained 70% solids prepared by dissolving 100 parts by weight of an epoxy resin (DER511), 4 parts by weight of a curing agent (Dicy), and 0.2 part by weight of a curing promoter (BDMA) in the solvents MEK and methyl glycol was applied to the above-mentioned polyamide resin-coated [*sic; "an aninosilane-treated" -- Tr. Ed.*] glass fabric base material so as to give an amount of resin of 30 parts by weight relative to 100 parts by weight of said base material, and the resulting product was heat dried to obtain a prepreg.

Eight sheets of this prepreg were then stacked and subjected to heat and pressure to obtain a laminate 1.6 mm thick.

Using this laminate as a substrate for a printed-wiring board, a two-step, wide printed-wiring board for a DEX-21 reliability examination as specified by Musashino Electrical Communications Laboratory, Nippon Telegraph and Telephone (Ltd.), was prepared by perforating the laminate, then applying copper plating to form a circuit.

Comparison Example 1

40 parts by weight of a polyimide resin (Kelimide 601) was used to impregnate 60 parts by weight of the same glass fabric base material used in the Actual Example and by the same method used in the Actual Example, and the resulting product was heat dried to obtain a prepreg. Eight sheets of this prepreg were then stacked and subjected to heat and pressure to obtain a laminate 1.6 mm thick. Then, using this laminate as a substrate, a printed-wiring

board for a DEX-21 reliability examination of the same dimensions was prepared as in the Actual Example.

Comparison Example 2

A prepreg was prepared by using 40 parts by weight of epoxy resin alone for the epoxysilane-treated glass fabric base material MIL7628 (Nittobo Co.), without the polyimide treatment of the Actual Example. The other conditions were similar to those of the Actual Example. Eight sheets of this prepreg were then stacked and subjected to heat and pressure to obtain a laminate 1.6 mm thick. This laminate was then used as a substrate to prepare a printed-wiring board for a DEX-21 reliability examination of the same dimensions as in the Actual Example.

An electrolytic corrosion test was carried out by applying 100 V continuously at 95% RH to the two-step, wide printed-wiring boards for a DEX-21 reliability examination as prepared by the Actual Example, Comparison Example 1, and Comparison Example 2.

The occurrence of CAFs was assessed in terms of a decrease in the insulation resistance of the printed-wiring board. The results are given in Figure 1.

Effect of the Invention

The test results of the Actual Example of the present invention are very close to those of the printed-wiring board treated with just a polyimide resin, as can be seen by the decrease in insulation resistance shown in Figure 1. As opposed to this, there is an extremely large decrease in the insulation resistance of Comparison Example 2 in which just an epoxy resin was used for

the treatment.

It can be seen that the electrolytic corrosion-resistance effect of the present invention is remarkable.

Furthermore, the ratio of the cost of the laminates for the Actual Example of the present invention, Comparison Example 1, and Comparison Example 2 was calculated. If we set the cost of Comparison Example 2 treated with just epoxy resin at 1, the cost of the Actual Example of the present invention is 3 and the cost of Comparison Example 1 treated with just polyimide resin is 8. In other words, the present invention not only provides excellent electrolytic corrosion resistance but is also promising in terms of manufacturing cost.

4. Brief Description of the Figure

Figure 1 is a graph which illustrates the electrolytic corrosion resistance of the printed-wiring board according to the present invention.

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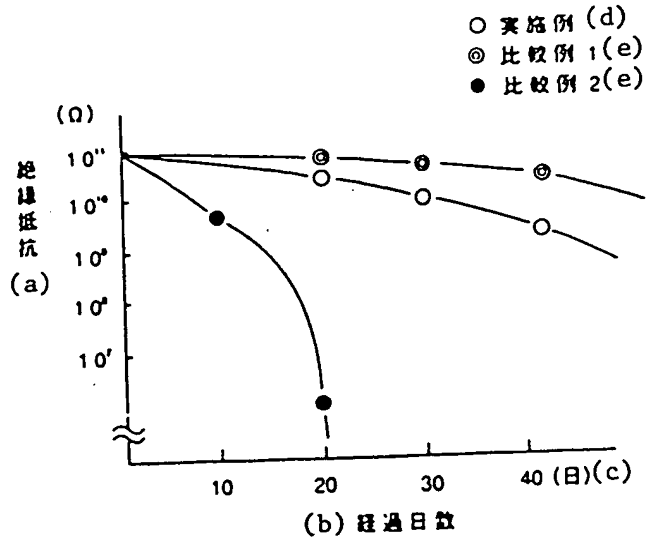

Figure 1. KEY: (a) insulation resistance, Ω; (b) number of days elapsed; (c) (days); (d) Actual Example; and (e) Comparison Example ....